Chemical Reaction Analysis Based on the SR Absorption Spectroscopy for the High Sensitive EUV Resist

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Outline

1. Introduction
   RLS, key points for EUV resist development, solvent effect

2. PAGs employed in the model resist for this experiment

3. Sensitivity differences in KrF, EB and EUV
   (TPS-nonaflate and TPS-IMIDATE employed as PAG)

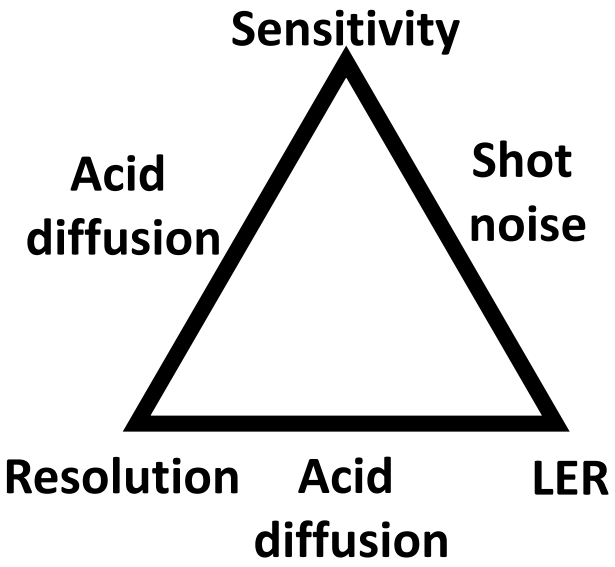
4. Results and discussions of outgassing analysis, FT-IR spectra analysis and computation analysis using Gaussian04.

5. Results and discussions of SR absorption spectroscopy measurement

6. Summary

EUV Resist issue (RLS trade off)

Specification of EUV Resist



Reduce affection of shot noise
⇒Increase acid generation quantum efficiency

→

Beneficial PAG for EUV resist

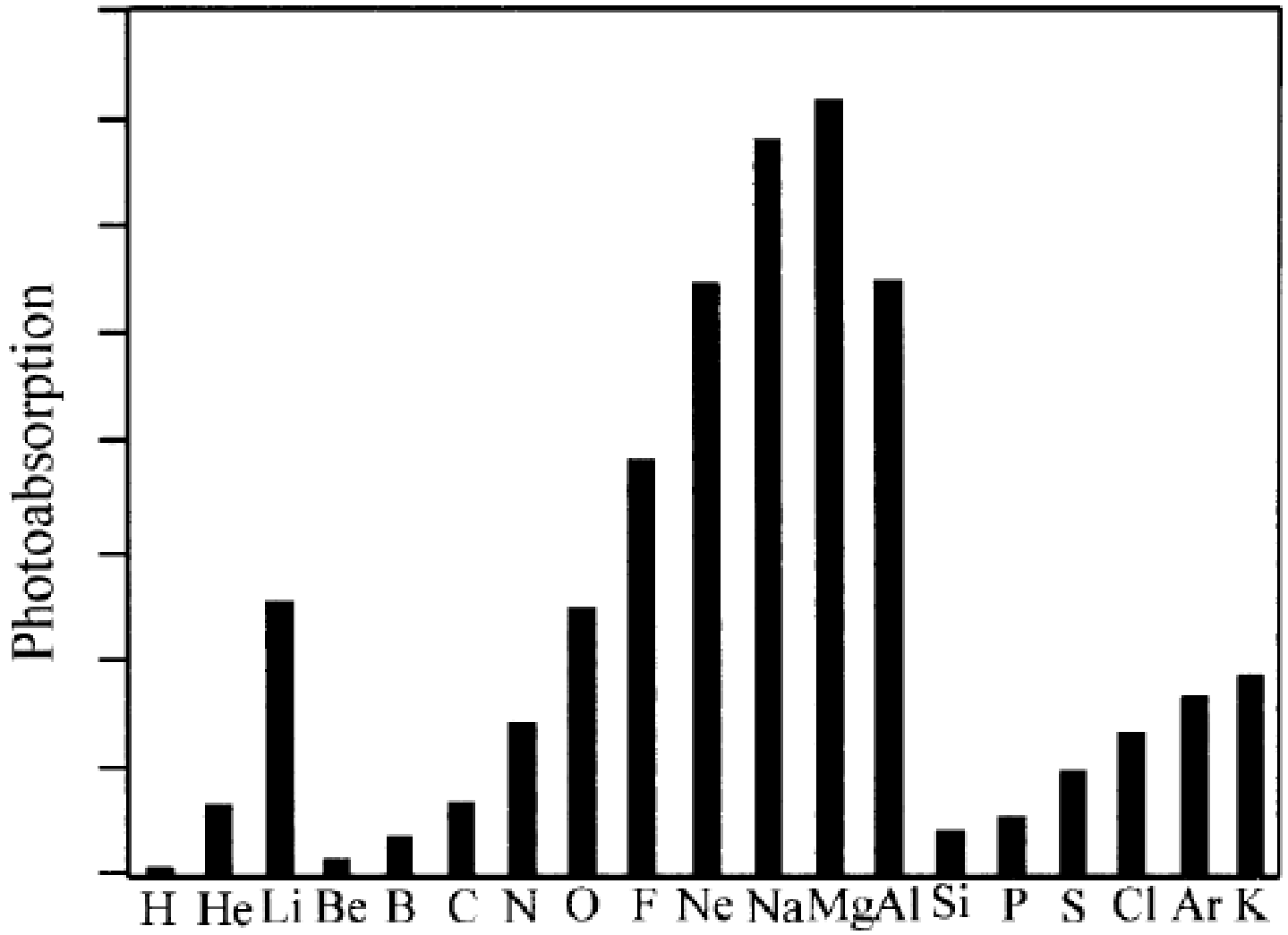
EUV resist development for 22 nm ~ 15 nm nodes

Isuue	Solution
Chemical Reaction in EUV	Ionization Molecular direct excitation Atomic direct excitation Acid production efficiency Absorption coefficient Resist blur
Resolution	Non chemically amplified resist Chemically amplified resist
LWR	Acid diffusion control Developer Chemical structure Molecular weight
Sensitivity	Photo chemical reaction efficiency Acid yield
Pattern Collapse	Under layer Decreasing surface tension in the rinse process
Outgassing	Base resin, PAG, protection group, solvent, top layer

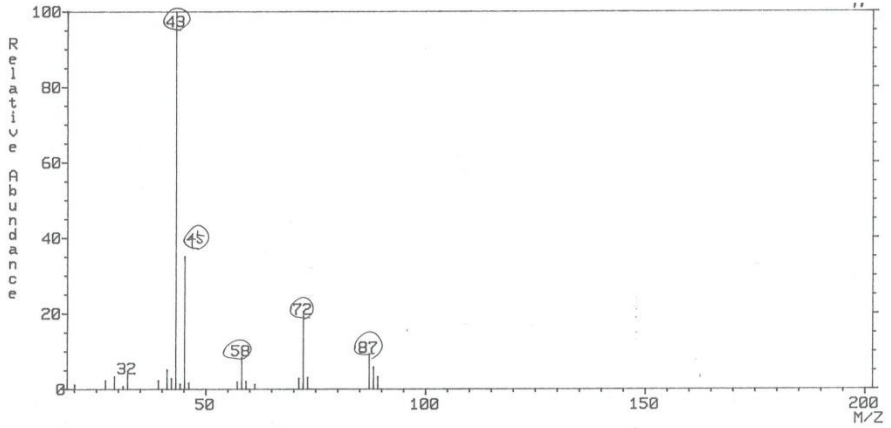
EUV resist development for 15 nm ~ 11 nm nodes

Isuue	Solution
Chemical Reaction in EUV	Ionization Molecular direct excitation Atomic direct excitation Acid production efficiency Absorption coefficient Resist blur
Resolution	Non chemically amplified resist Chemically amplified resist
LWR	Etch trim and shrink process Acid diffusion control Developer Chemical structure Molecular weight
Sensitivity	Photo chemical reaction efficiency Acid yield
Pattern Collapse	Under layer Decreasing surface tension in the rinse process
Outgassing	Base resin, PAG, protection group, solvent, top layer

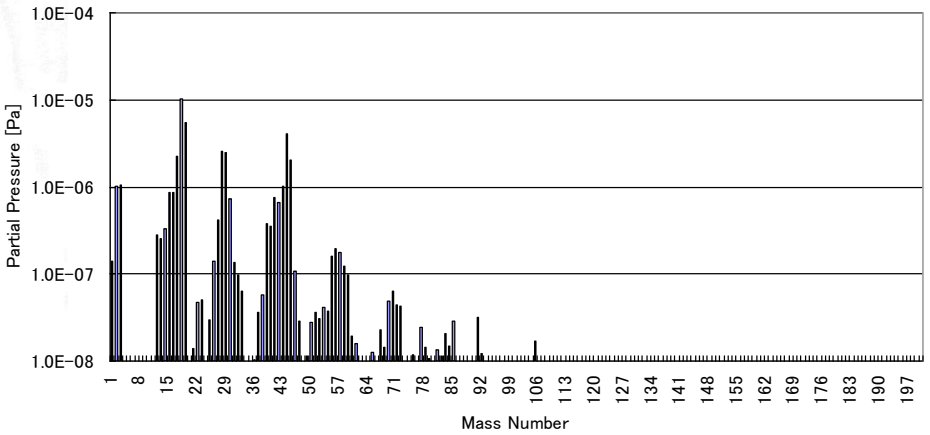
Photoabsorption of the main elements for the resist



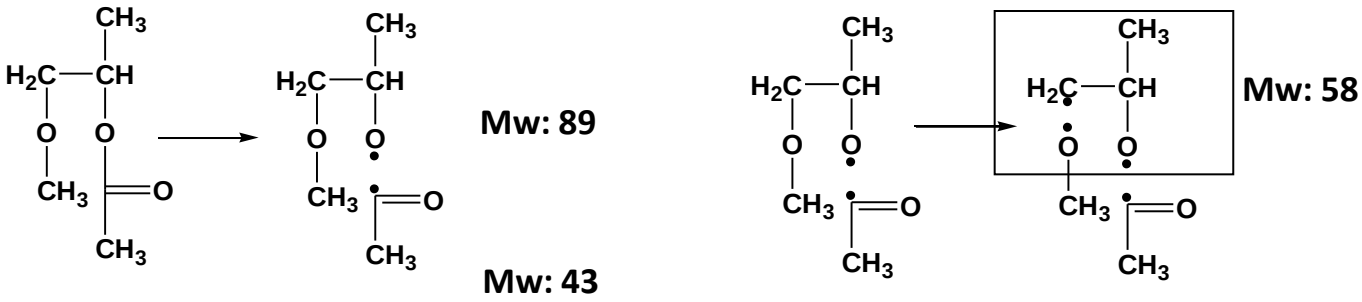
Decomposition analysis of PGMEA in EUV lithography



(a) Fragments from GC-mass

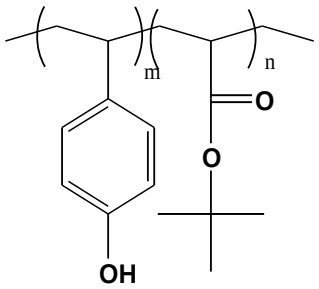
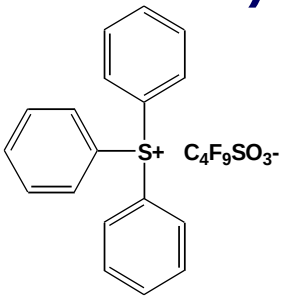
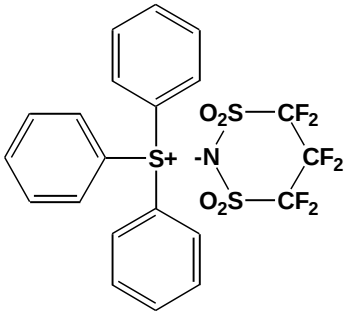


(b) Partial pressure displacement

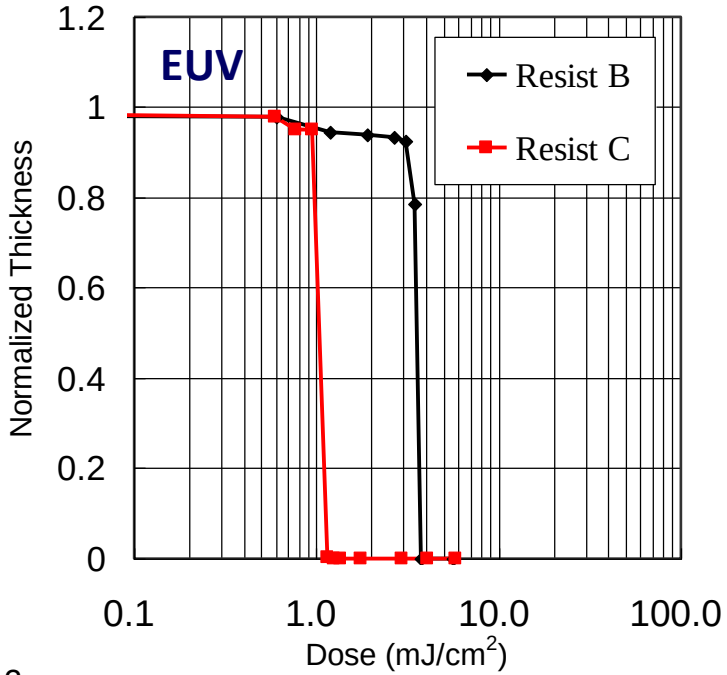


(c) Decomposition reaction of PGMEA in resist

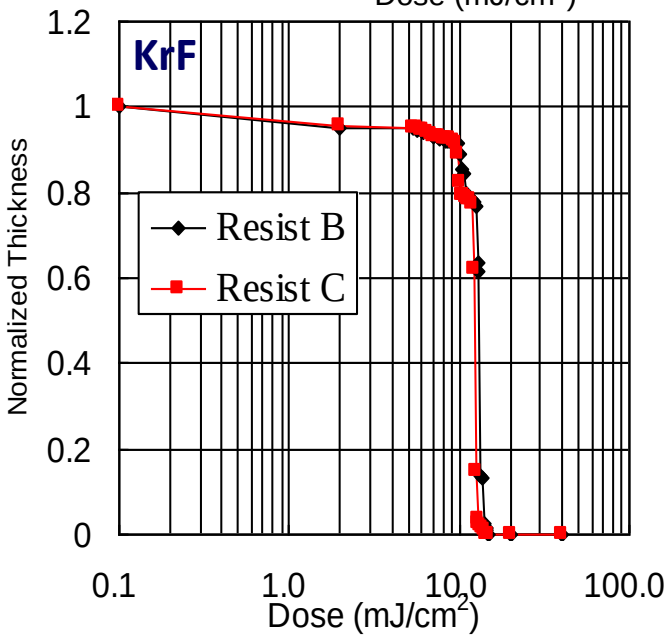
Resist samples employed in the experiment of PAG effect

Sample	Resist A	Resist B	Resist C
Base polymer	 poly (vinylphenol-co-tert butylacrylate)		
PAG	None	TPS-PFBS (10 wt% Ref.) 	TPS-IMIDATE 
Solvent	propylene glycol monomethylether acetate (PGMEA)		

Eth differences under between EUV, KrF, and EB exposures



Sample	Sensitivity
Resist B	3.8 mJ/cm²
Resist C	1.1 mJ/cm²



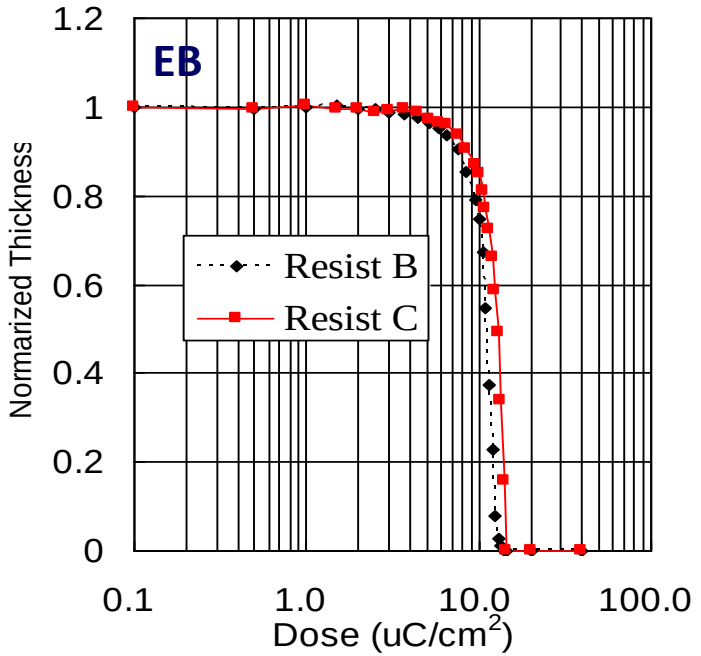
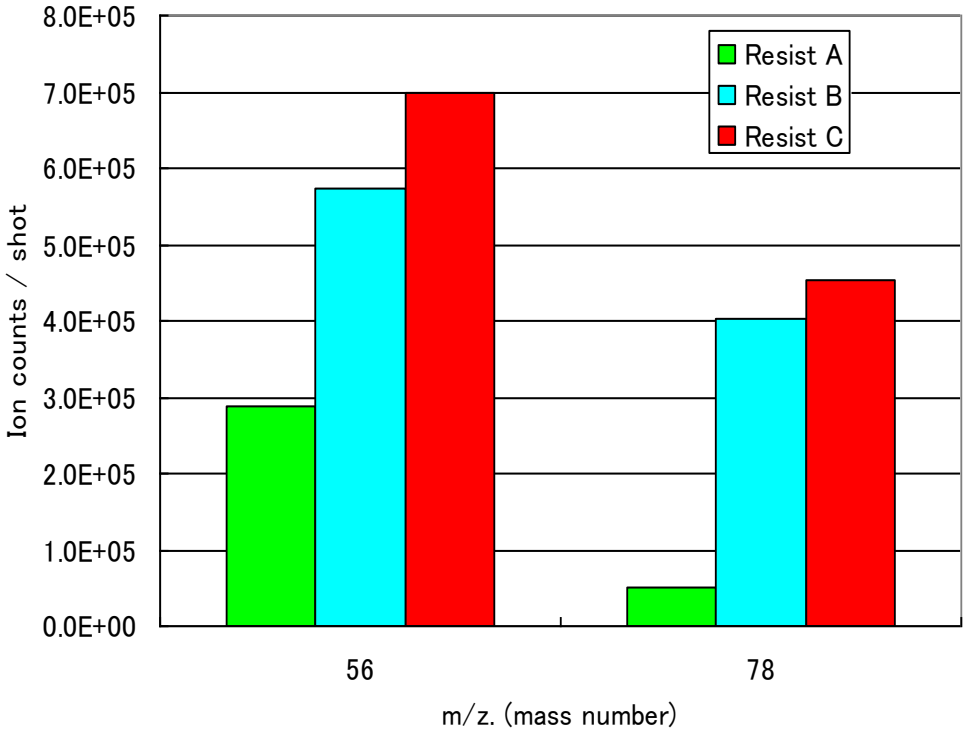


Photo decomposition reaction of cation of PAG in Resists B and C

m/z = 56
(isobutene)

m/z = 78
(benzene)



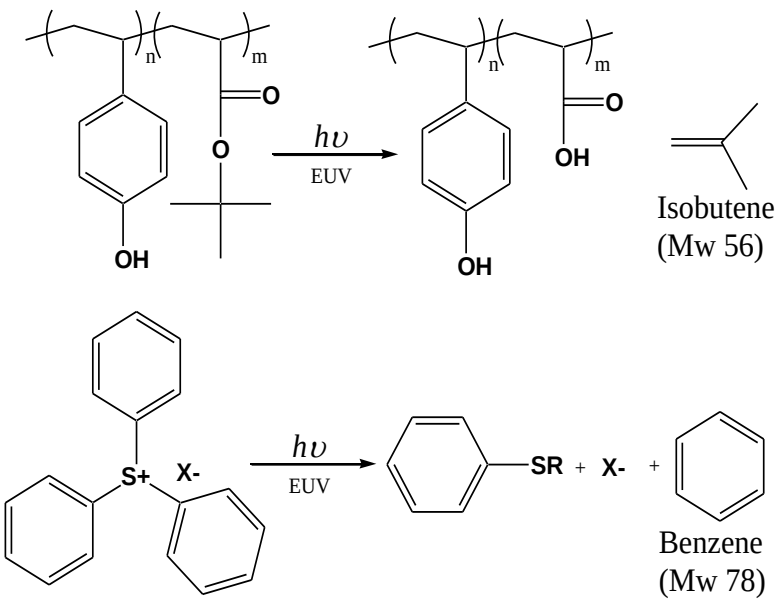
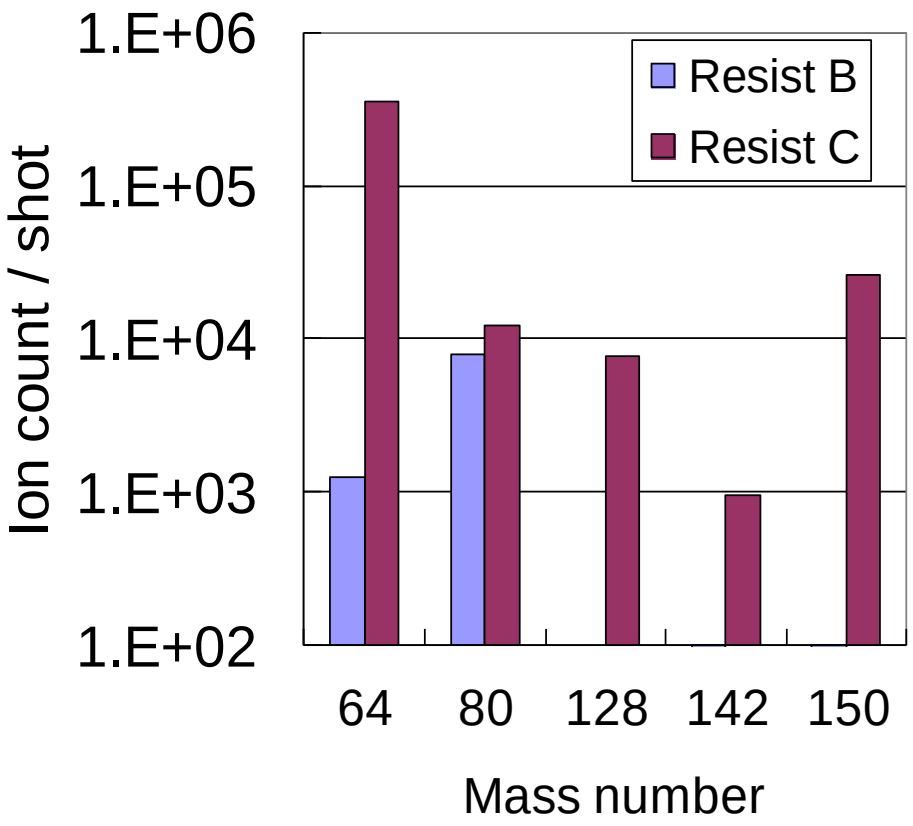
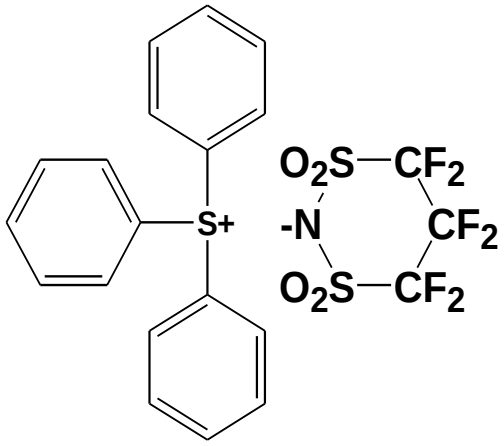


Photo decomposition species of anions of PAGs

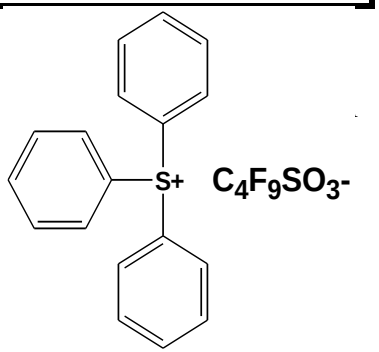


m/z	Speices
64	SO_2
80	SO_3
128	CF_2SO_2N
142	SO_2-N-SO_2
150	$(CF_2)_3$-

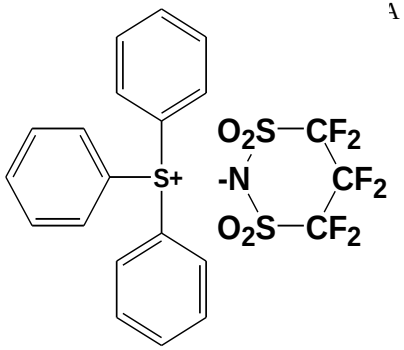


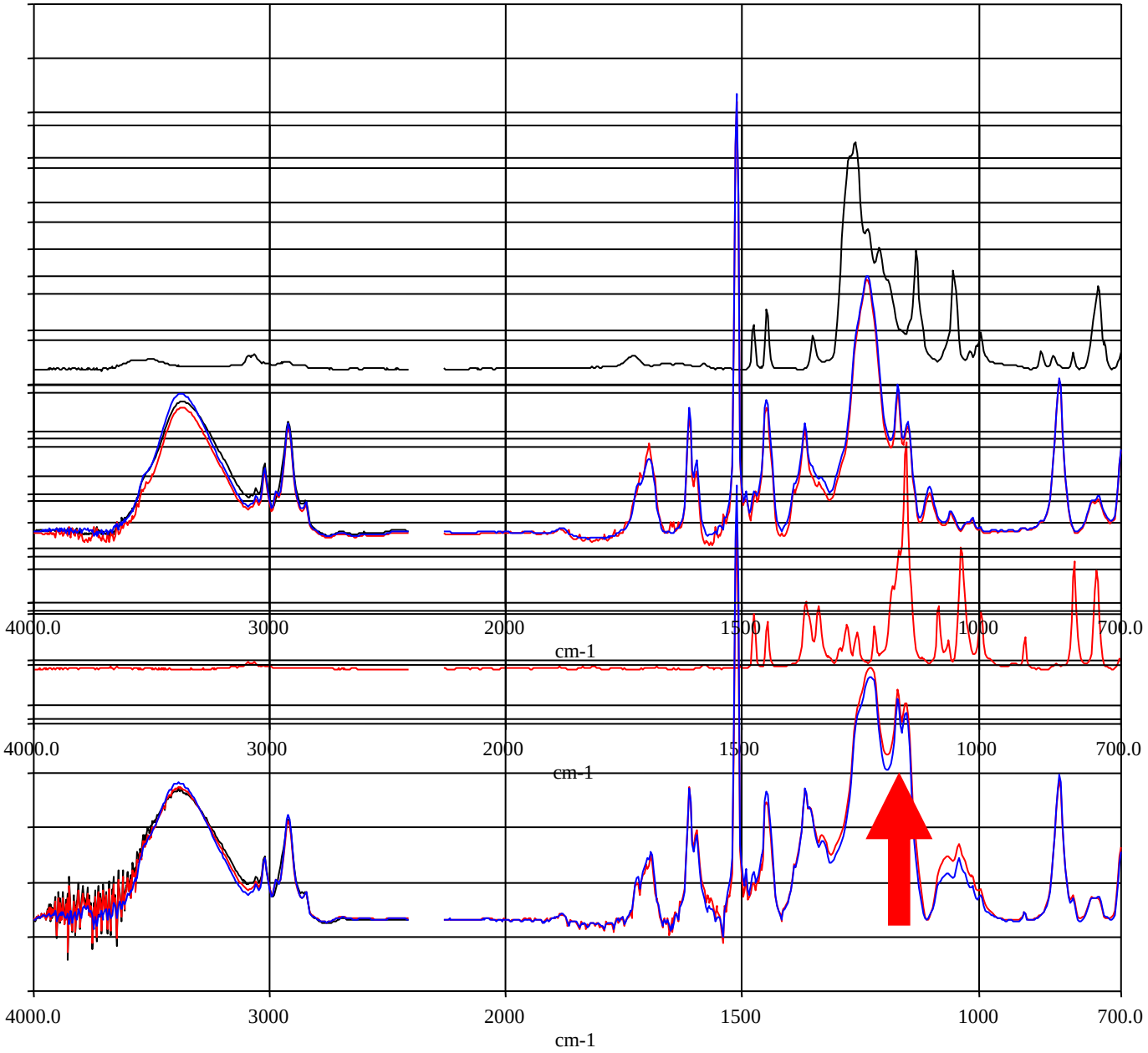
FT-IR spectra of Resists B and C

Resist B

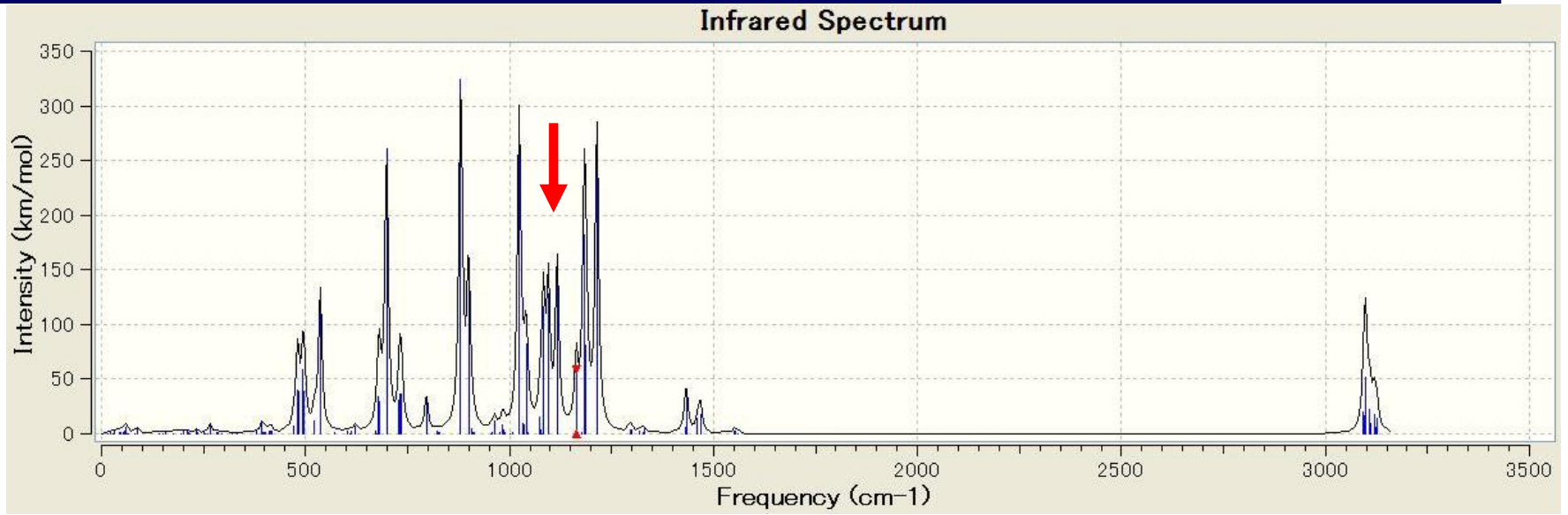


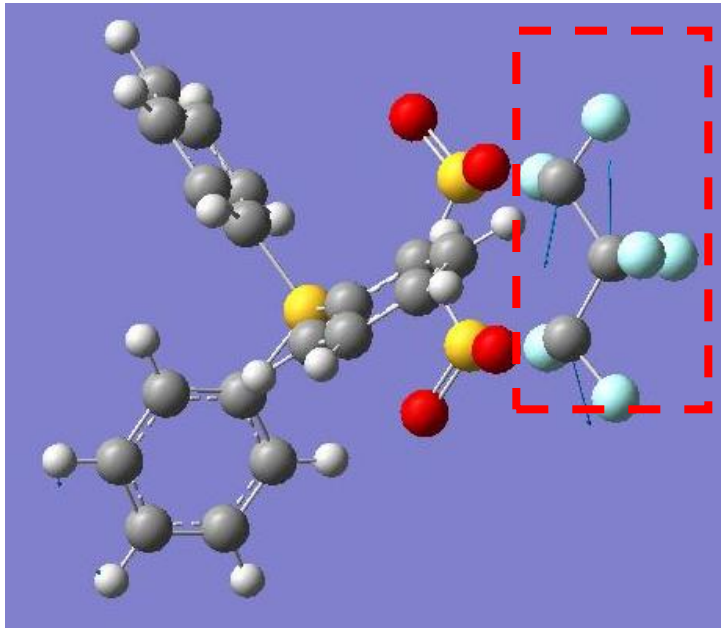
Resist C



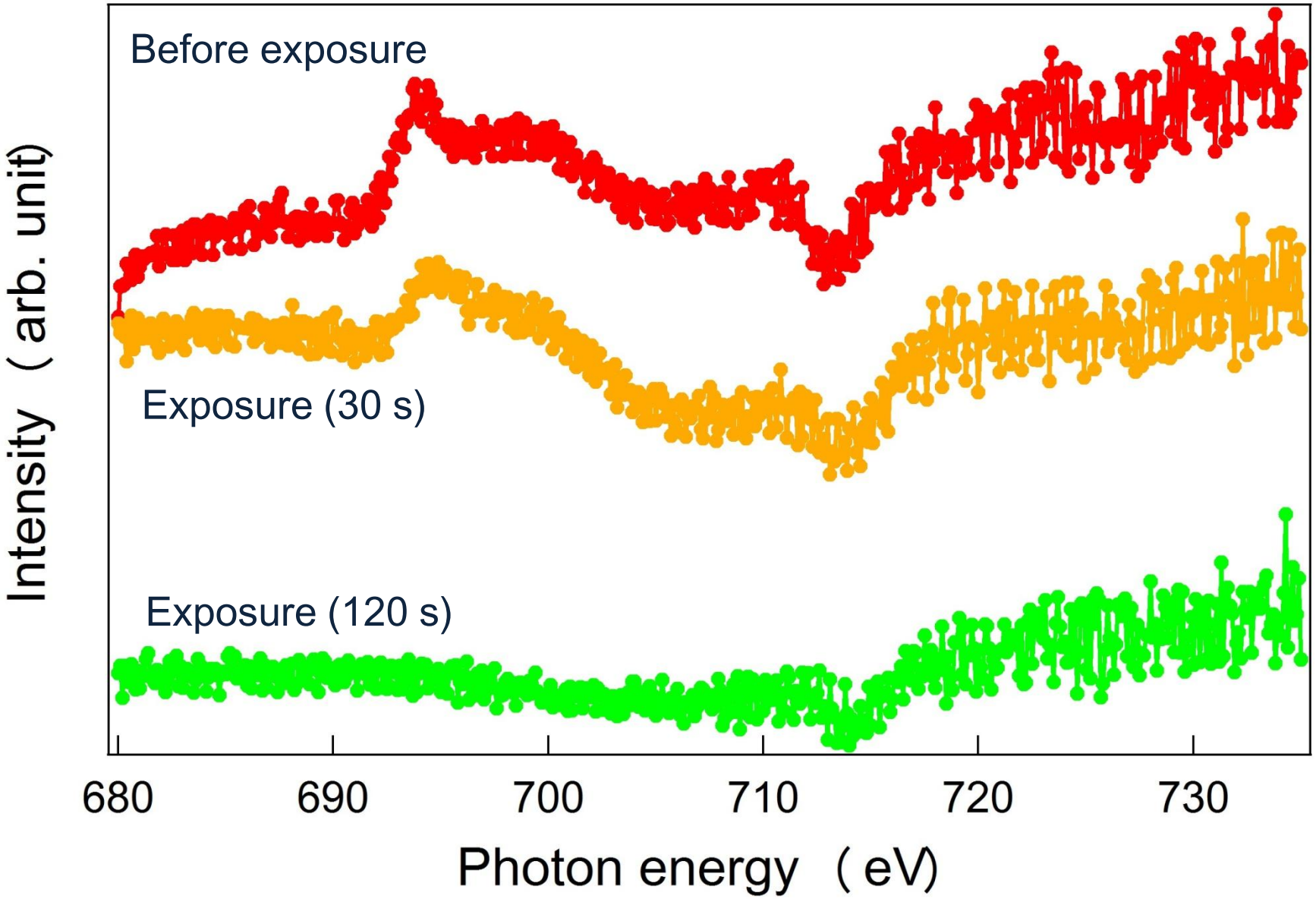


The computation results of the infrared spectrum by the molecular orbital calculation on the basis of the perturbation theory using the software code Gaussian04

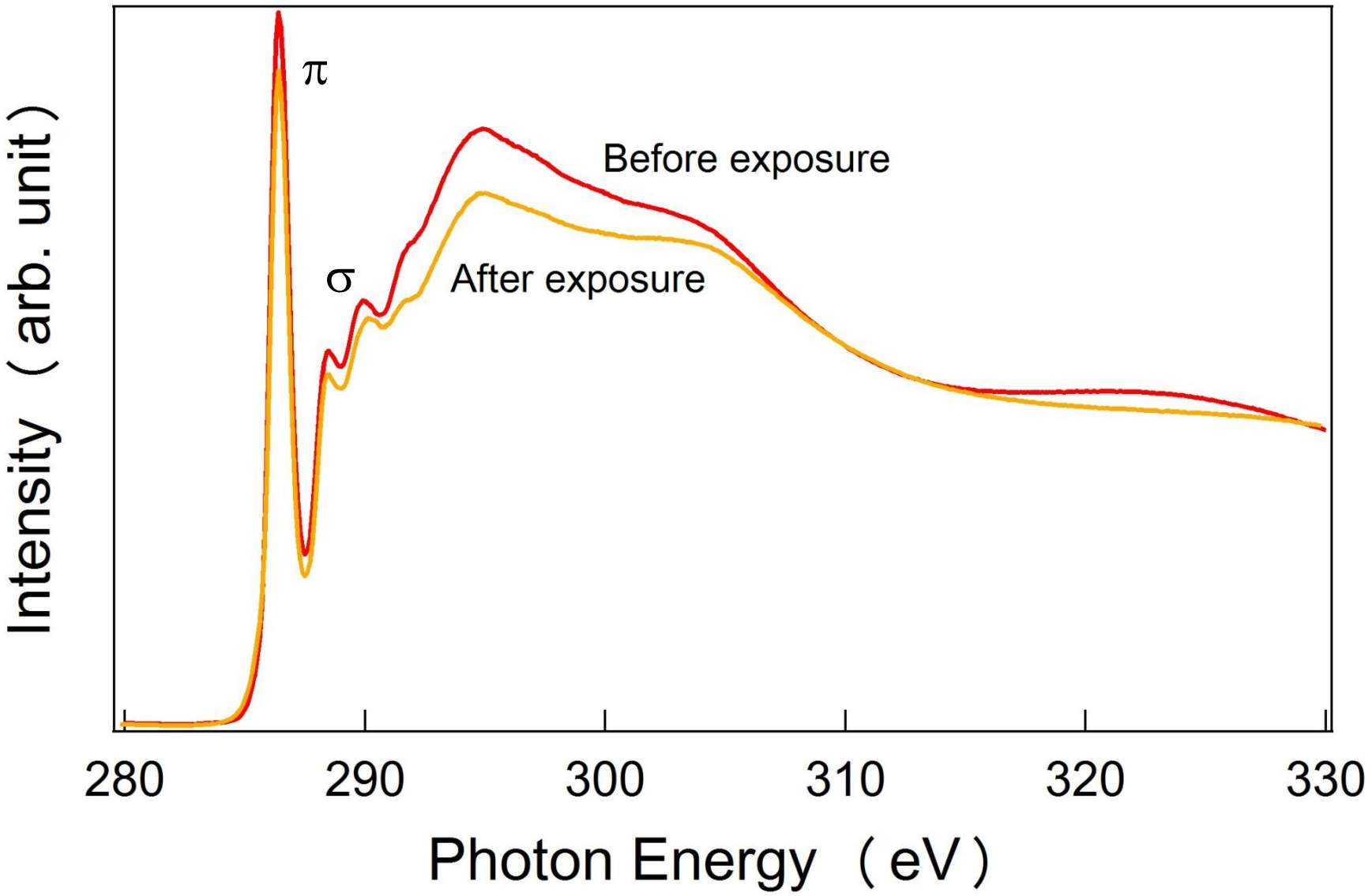




Exposure dose dependency of the absorption spectra of fluorine 1s core level in the anion of TPS-IMIDATE



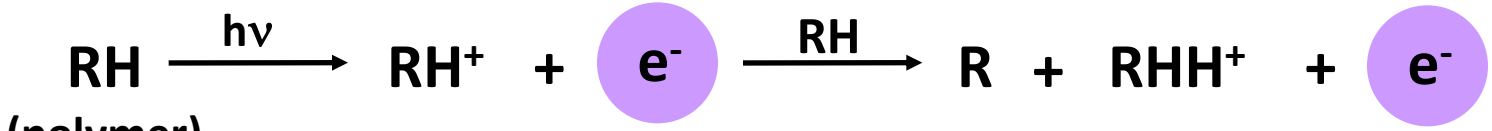
Exposure dose dependency of the absorption spectra of carbon 1s core level of TPS-IMIDATE

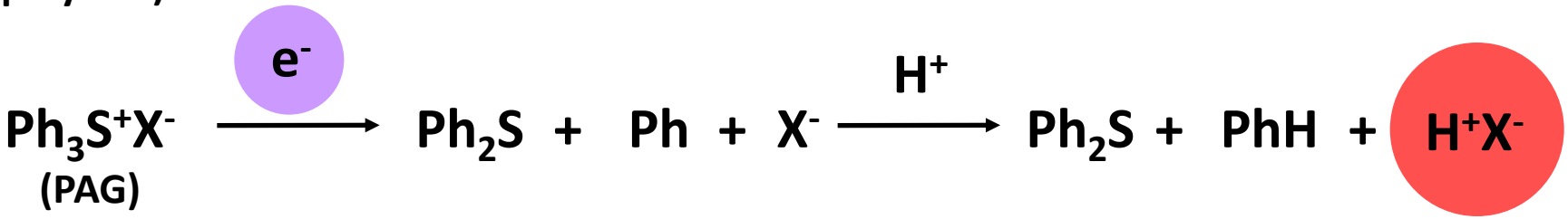


Acid generation mechanism (Ionization)

Secondary electron

(Base polymer)



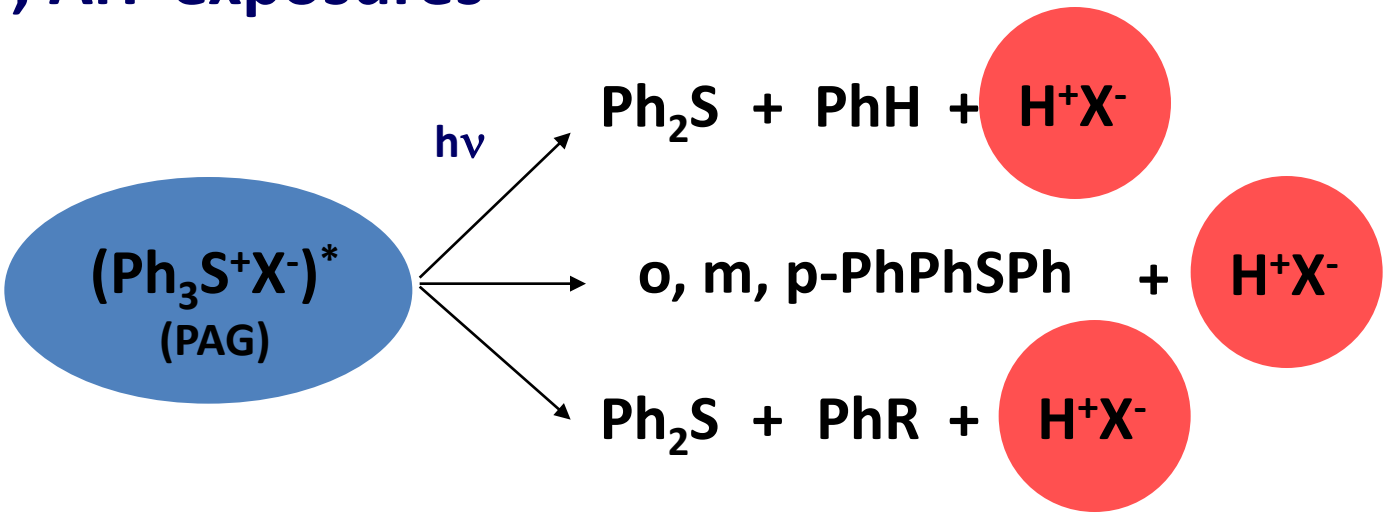


By S. Tagawa and T. Kozawa. Osaka University

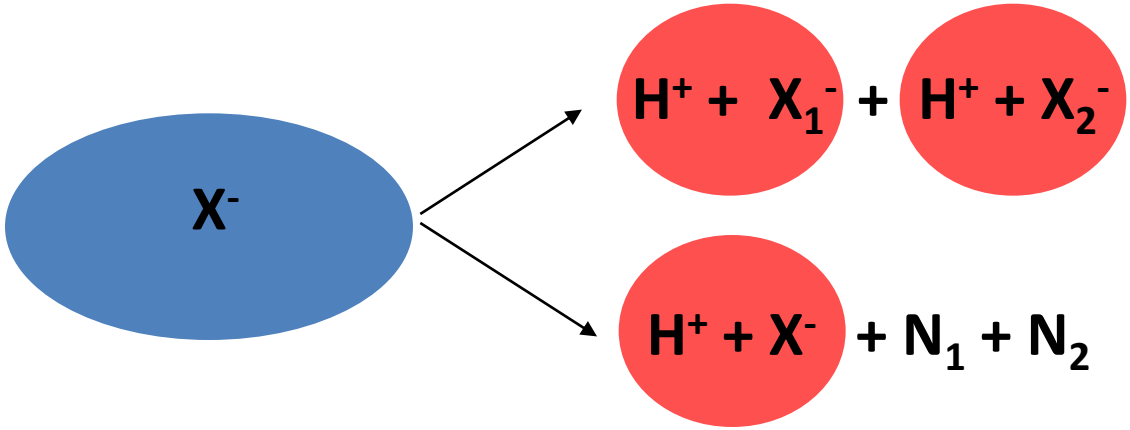
Anion effect of PAG

Excitation reaction

KrF, ArF exposures



EUV exposures



Summary

1) In EUV irradiation, the sensitivity of CA resist which employs TPS-IMIDATE as a PAG is 4 times higher than that which employsTPS-nonaflate as a PAG.

2) In Krf and 75 keV EB irradiation, there were no sensitivity differences between TPS-IMIDATE and TPS-nonaflate.

3) The higher sensitivity due to the decomposition of the anion of TPS-IMIDATE in EUV irradiation.

4) Therefore, not only the ionization reaction but also the PAG excitation might be occurred. If we take in count both reactions for the design of a EUV resist, the specification of the sensitivity might be satisfied.

Anion effect of PAG

Photoacid generator (PAG)

$$PAG \xrightarrow{h\nu} Cation + (\underbrace{P_1^+ + P_2^+ + X_1^- + X_2^- + X_3^-}_{\text{Anion of PAG}})$$

Acid multiple production

$$PAG \xrightarrow{h\nu} \begin{cases} H^+ + X1^- \\ H^+ + X2^- \\ H^+ + X3^- \end{cases}$$

Absorption photon energy of the chemical elements

Z	Element	K(1s)	L3(2p)	L2(2p)	L1(2s)	M5(3d)	M4(3d)	M3(3p)	M2(3p)	M1(3s)
1	H	13.6								
2	He	24.6								
3	Li	54.7								
4	Be	111.7								
5	B	188.0								
6	C	284.2								
7	N	409.9			37.3					
8	O	543.1			41.6					
9	F	696.7								
10	Ne	870.2	21.6	21.7	48.5					
11	Na	1070.8	30.4	30.4	63.5					
12	Mg	1303.0	49.5	49.9	88.6					
13	Al	1559.6	72.7	73.1	117.8					
14	Si	1838.9	99.8	100.4	149.7					
15	P	2145.5	135.0	136.0	189.0					
16	S	2472.0	162.5	163.6	230.9					
17	Cl	2822.4	200.0	201.6	270.2					
18	Ar	3205.9	248.4	250.6	326.3			15.8	15.9	29.3